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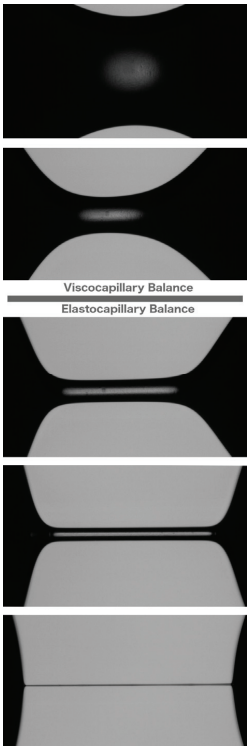

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EDITORIAL

Welcome to Volume 57 (issue #3) of the British Society of Rheology Bulletin. We have a packed issue, including an article from last year's annual award winner, Prof. Christian Clasen. Rob Poole's article on measuring normal stresses in the previous issue has drawn much interest, resulting in a clarifying "Letter to the Editor" from Rob.

The BSR council has recently aimed to encourage applications for our Student Travel Awards by relaxing the rules, and by lifting the limit on the number of such awards. This, coupled with an attractive location for the ICR meeting in Kyoto, resulted in no less than *seven* students being granted awards to travel to this conference – *a triumph*! But, since each awardee is supposed to write a short piece on the conference for the Bulletin, this presents your editor with a small problem of scale. I give you three reports this issue, with four more to follow next.

As always, I'm very pleased to receive submissions, comments and letters for upcoming issues!

Daniel Read, Leeds, November 2016.

SUBMISSIONS TO THE BULLETIN

Submissions to the Bulletin are welcomed. Electronic submissions by email to the Editor (bulletin@bsr.org.uk) are preferred in word format (e.g. .doc or .docx). Please always provide a contact name, address, e-mail, or telephone number in case of problems. The deadline for submission is Feb. 15th, July 15th and Oct. 15th, respectively, for three issues annually.

COVER ILLUSTRATION

The cover image is a CaBER experiment of a solution of 20 wt% of a 10 kg/mol poly (ethylene oxide), bi-functionalized with terpyridine, mixed in a stoichiometric balance with cobalt ions, courtesy of Wouter Mathues, Taisir Shahid, Jan Hendricks, and Christian Clasen. See Prof. Clasen's article for more details.

Citation: Professor Christian Clasen

The 2015 Annual Award of the British Society of Rheology was presented to Professor Christian Clasen at the Glasgow Midwinter Meeting in December 2015, for his contributions to experimental rheology. Christian, who is based at KU Leuven, has been a regular supporter of BSR meetings and has presented some of his work at several of the INNFM spring meetings in Vyrnwy and Port Meirion.

Christian began research as a PhD student of Werner Kulicke in Hamburg. As part of his thesis he built a very elegant two-color birefringence system and used it to study the properties of a number of polymeric fermentation products. Christian then moved to MIT to work with Gareth McKinley, who recalls him giving a nice talk on the 'birefringence of beer' to the group when he arrived. He worked with Gareth from 2001-2003, where he worked on constructing a unique flexure-based microgap rheometer (FMR) that was used to study the rheology of biopolymeric liquids such as spider silk or silkworm silk for which only very small samples were available, as well as foodstuffs (such as mayonnaise) for which the length scales of the microstructure and the flow (i.e. the gap clearance) interact.

He has spent his career beyond MIT at KU Leuven and has continued his impressive experimental efforts there; working on electrospinning, jet break up problems and designing a new improved version of the microgap rheometer that also enables normal forces to be measured using a rebalance technique. He is an outstanding thesis advisor and mentor to students, always willing to spend long hours with students in the lab (leading by doing) and offering clever suggestions on how to deal with the inevitable experimental difficulties encountered in research.

He leads the organization and implementation of the famed European Rheology School every September, and has very recently become the Rheology Group Leader at Leuven following Jan Vermant's departure for ETH.

He also holds a unique place in the world-wide rheology community: he is the only winner (to date) of both the SOR Publication Award (for a joint piece of work in 2007 with Chris Macosko and Skip Scriven's group in Minnesota regarding extensional rheology of very dilute polymer solutions) and the newly-instituted Rheologica Acta publication award (which was awarded for the first time in Spring 2015 in Nantes). This latter work was carried out with Damien Vadillo (a former postdoctoral collaborator of Malcolm Mackley's at Cambridge) and focused on quantitative extraction of relaxation times for very dilute solutions. The initial data was obtained at the end of Vadillo's thesis, on weakly viscoelastic printing inks and Christian figured out a clever data analysis approach using high speed digital video analysis and automated edge detection algorithms that allowed his graduate student Wouter to measure relaxation times down to sub 100 μs values. This is a

truly outstanding piece of experimental work that has pushed the capillary thinning technique into brand new territory, and which is of great relevance to the drop-on-demand inkjet printing community.

Gareth McKinley, who nominated Christian for the Award, says: "Christian is an outstanding experimental rheologist who has, what Gerry Fuller and I refer to as, 'the knack' (or a rheological green thumb); essentially he can make any piece of experimental apparatus 'sing', and perform beyond its greatest potential. He combines this skill with a very Germanic work ethic and his papers are characterized by compendious data sets that are precisely analysed and immaculately presented. When he was a postdoc in my group, in addition to his primary experimental focus, because of his gregarious and open nature Christian also became directly involved with a large number of other projects in my lab including triborheometry, digital videoimaging and modeling beads-on-a-string structures on polymeric jets and threads, and developing new protocols for large amplitude oscillatory shear (LAOS) on snail mucins. We have continued to collaborate constantly since he left MIT and he returns to the Hatsopoulos Lab at MIT regularly. My lab will always be open to him because of his open collaborative nature and approachability to students."

Helen J. Wilson
BSR President

An analytical solution for the initial polymer stretch evolution in thinning viscoelastic filaments

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It is an understatement to say that I felt honoured to contribute a short article to the BSR Bulletin in return for receiving the Society's 2015 Annual Award and immediately agreed to do so. It only came to me later that this is, actually, not an easy task. You don't want to just deliver a nice, easy reading piece about how great rheology is and what this award meant to one's career and research. Instead, I felt obliged to contribute something new and useful to the rheological community. However, the format of the bulletin does not really allow a text of the size of a full journal paper and even a full review was out of the question. This left me with the predicament of finding a nice little problem that remains unsolved (or, in particular, has not been published elsewhere), can be presented in a few pages and still have a bit of an impact. This took a while and I wore out two Bulletin editors on the way before I finally wrote this paper. Luckily, I do have some smart PhD students and, as it turns out, they often come up with ideas, observations or solutions that progress our daily research, but that are, by themselves, not the key

message of a paper and thus often vanish as appendices (or "lab knowledge" that does not get published at all). So, I took the liberty of picking one of those ideas and turning it into this article to give it a little more publicity (and of course added the students that came up with this and did the real work as co-authors!).

The following problem came up when we were reading and reviewing a nice paper by Caroline Wagner *et al.*, entitled "An analytical solution for capillary thinning and breakup of FENE-P fluids" [1] in which they present an analytical solution for calculating breakup times of viscoelastic liquid filaments of dilute polymer solutions. Such breakup times are important parameters for practical applications, from inkjet printing to general dispensing or filling operations. One usually observes for such filaments an initial fast decrease of the filament radius R followed by a sudden decrease in the thinning speed due to the fluid's elasticity before the filament finally breaks (see Fig. 1 for the typical shape of such a diameter evolution, and the cover of the bulletin for a series of images of such a thinning filament).

Wagner *et al.* described the overall process by combining two known thinning dynamics: an initially fast thinning of an instability developing on a liquid filament that is dominated by a viscocapillary balance (and described in detail in [2,3]) and the subsequent slower thinning controlled by an elastocapillary balance (which has been initially described using a FENE-P model in the landmark paper of Entov and Hinch [4]). In principle, the filament evolution can be determined numerically (when the fluid parameters as viscosity η surface tension γ, extensional relaxation time λ and finite extensibility parameter Z of the polymer are known) by solving a set of coupled ODEs arising from the evolution equations of the FENE model that involve the polymer stretch in form of the microstructural deformation tensor **A** (an example is shown in Figure 1) [5].

However, setting up this calculation is a tedious process and not quickly accessible to everybody who simply wants to do a quick calculation of the lifetime of such a filament. Here lies the beauty and (for me at least) most important message of the paper of Caroline Wagner *et al.*: in their equation (10), they present for the first time an *analytical* solution for the elastocapillary thinning regime that incorporates finite extensibility [1]. Although they never explain *how* they obtained this solution, this equation can now be used to directly predict the breakup time! The only thing that remained was to match this solution to the initially fast filament thinning, which was controlled only by the viscosity. Wagner *et al.* have accomplished this by calculating the evolution of the polymer stretch in this first regime, again using the FENE model, up to the point that the stretched polymers deliver sufficient stress to cause the transition to the elastocapillary balance regime. An analytic solution was also provided for this region, so that the entire evolution of the filament diameter can be described with an analytical solution (although the

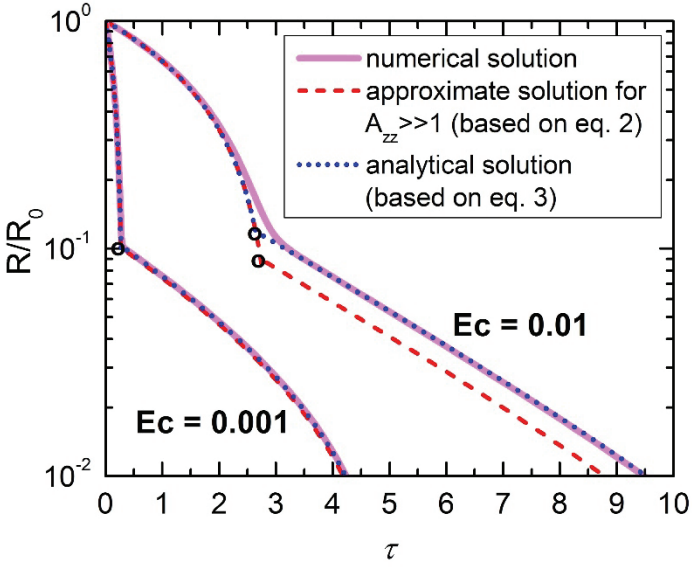

Figure 1. Evolution of the radius R of viscoelastic liquid filaments (reduced by the initial radius) as a function of the dimensionless time $\tau = t/\lambda$, for a relatively low elastic contribution (elastocapillary number Ec = 0.001), and a case (Ec = 0.01) where elasticity can no longer be neglected. The approximate and analytical solutions are calculated based on Eq. (2) and (3), respectively, for times up to the hollow circles. The solutions for the elastocapillary balance regime after the hollow circles are calculated using the analytical solution of Wagner et al. [1].

matching of the two regimes lead to an implicit solution for the diameter).

This brings me to the point of our small contribution in this article: The onset of the analytic solution of Wagner *et al.* for the elastocapillary balance regime, this transition point between the fast viscous and the slower elastic regime marked with a hollow circle in Fig. 1, depends on the evolution of the microstructural deformation tensor **A** in the initial viscous regime. Using the evolution equation for the axial component of **A** from the FENE model

$$\dot{A}_{ZZ} = 2\dot{\varepsilon}A_{ZZ} - \frac{1}{\lambda}(ZA_{ZZ} - 1) \qquad (1)$$

which allows the required temporal evolution of A_{zz} for a known evolution of the extension rate $\dot{\varepsilon}$ to be determined. A simple solution can be obtained by making two major assumptions, namely that axial component of the stretch of the polymer

along the filament axis $A_{zz} >> 1$ and that the finite extensibility parameter $Z = 1$. In this case (and for a know viscosity dominated extension rate $\dot{\varepsilon} = 2/(\tau_p - \tau)$), one obtains a simple solution of the form

$$A_{ZZ} = \left(\frac{\tau_p}{\tau_p - \tau}\right)^4 e^{-\tau} \quad (2)$$

where $\tau = t/\lambda$ is the time (non-dimensionalized using the relaxation time λ), and $\tau_p = t_p/\lambda$ is the non-dimensional time to breakup of a purely viscous filament. Use of the assumption that $A_{zz} >> 1$ can be traced back to the paper of Entov and Hinch, where they utilized a similar approach to find their general solution for the elastocapillary balance regime [4]. In their case, this could be easily justified since the polymer chains needed to be sufficiently stretched to be able to deliver enough stress for the occurrence of an elastocapillary balance, so that indeed $A_{zz} >> 1$ for the onset of this regime.

However, for the calculation of the evolution of stretch for a polymer coil in the initial regime, we usually start with a fully relaxed coil, for which $A_{zz} = 1$. So, in particular, when the fluid's elastocapillary number $\text{Ec} = \lambda R/\eta\gamma$ (which compares elastic to viscous contributions in the filament) is large, assuming that $A_{zz} >> 1$ for all times when deriving an analytical solution will strongly affect the calculated evolution of the polymer stretch at early times. This can clearly be seen in Fig. 2, which compares the evolution of A_{zz} for this simplified case to the exact solution of the numerical simulation for Ec = 0.01. The simplified solution underestimates A_{zz} and, as a result of this, over-predicts the time at which the elastic stresses have grown sufficiently to balance the (filament radius and thus also time dependent) capillary pressure. This transition point between the fast viscous and the slower elastic regime is also marked with hollow circles in Fig. 2.

The shift of the transition point also has a strong impact on the final breakup time as can be seen in Figure 1. Since the elastocapillary balance has a much slower thinning, even slight shifts of the onset point in time will lead to an amplified underestimation of the breakup time from the simplified solution (dashed line in Figure 1) due to the much slower thinning in the elastocapillary balance regime.

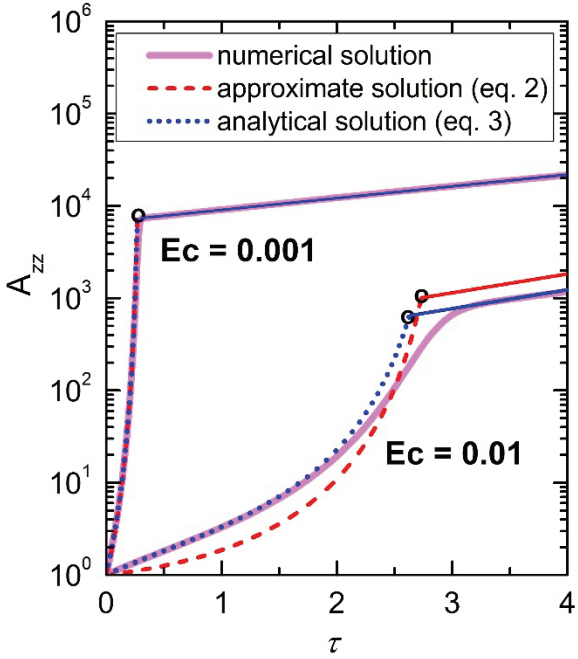

Figure 2 Evolution of the axial polymer stretch A_{zz} with time for two different elastocapillary numbers Ec. The exact numerical solution of Eq. (1) is compared to the approximate solution of Eq. (2) and the new analytical solution of Eq. (3) (up to the hollow circles that mark the transition to the elastocapillary balance regime).

However, there is hope. Below, we present an exact *analytical* solution of Eq. (1) for the evolution of the polymer stretch A_{zz} in the initially viscosity controlled regime without making assumptions on A_{zz} (but still assuming that $Z = 1$, which is justified as we start from $A_{zz} = 1$). Following the tradition of Wagner *et al.*, we are going to present this as *ad hoc* as they have been presenting their solution, so:

$$A_{ZZ} = \frac{\begin{pmatrix} (\tau_p - \tau)^4 + 4(\tau_p - \tau)^3 + 12(\tau_p - \tau)^2 \\ +24(\tau_p - \tau) + 24 - \left(4\tau_p^3 + 12\tau_p^2 + 24\tau_p + 24\right) e^{-\tau} \end{pmatrix}}{(\tau_p - \tau)^4}. \qquad (3)$$

A comparison of this solution (dotted line in Fig. 2) to the full numerical simulation shows not only an excellent agreement of A_{zz} right from the beginning, but also a much more realistic prediction of the transition point, so that also the filament radius evolution in the subsequent elastocapillary balance in Fig. 1 shows an excellent agreement to the numerical simulations.

Finally, it should be noted that for solutions with a lower elasticity (and thus lower Ec numbers), the simple solution also simplifies to the exact solution of eq. (3) and the full numerical simulations. This can be seen in both Figs. 1 and 2 where, for the case of a lower Ec = 0.001, the simple and the full solution match.

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Letter to the Editor

Dear Editor,

Further to my recent article in the *Rheology Bulletin* Volume 57, issue 2, "Measuring normal-stresses in torsional rheometers: a practical guide", Professor Morton Denn (Albert Einstein Professor of Science and Engineering Emeritus, of City College of New York) has made me aware that the parallel-plate device is more robust than indicated in my Eq. (5). This is because the Reynolds number is, in fact, $\rho\omega h^2/\eta$ for large R/h [1-2], so there is an h-squared dependence and no dependence on R (meaning of symbols same as in original article). Thus, in recommending to use the device with small gaps, the Reynolds number can become even smaller than proposed (as h can be typically ~$0.01R$).

I'd like to take this opportunity to formally thank Prof. Denn for bringing this issue, and the relevant papers, to my attention.

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Yours sincerely

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